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THE STRUCTURE OF THE AZOXY
GROUP

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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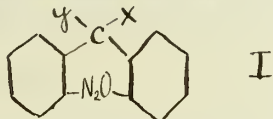
To Dr.C.S.Marvel,whose suggestion formed the guiding idea in this investigation,whose help was instrumental in carrying out that idea,and whose encouragement was a constant source of inspiration,the author gratefully expresses acknowledgment and appreciation.

TABLE OF CONTENTS.

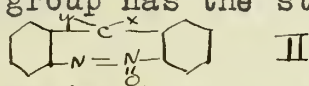
	Page
Introduction	1
Historical and Theoretical	2
Preparation of Nitrogen Pentoxide	5
Preparation of Acetylnitrate	6
Attempted Nitration of Benzilic Acid with Acetylnitrate .	6
Preparation of Diphenylacetic acid	7
Nitration of Diphenylacetic acid with Acetylnitrate . . .	8
Preparation of Benzhydrol	9
Action of Hydrobromic acid on Benzhydrol and Benzhydrol Ethers	12
Action of Hydrochloric acid on Benzhydrol and Nitration of the Product	13
Preparation of Diphenylbrommethane and its Nitration . . .	14
Preparation of p,p,diamino-diphenyl-methane and Nitration.	15
Preparation of the p,p,dibrom- and p,brom-p,hydroxy derivatives of o,o',dinitro-diphenyl-methane	16
Attempted Oxidation of p,p,diamino-o,o',dinitro-diphenyl- methane	18
Action of Chromic Acid on the Amine Hydrochloride	19
Preparation of the Diacetyl Derivative of the Amine . . .	19
Attempted Oxidation of the Diacetyl Derivative	19
Summary	21
Bibliography	22

INTRODUCTION.

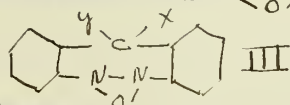
Before the time of the work of A. Angeli and his co-workers, there was relatively little experimental evidence for establishing the structure of the azoxy group. The work of Angeli showed rather conclusively what the structure is, yet there seems to be some points lacking to make the proof complete. The following investigation was carried out in hope of offering another and perhaps wholly conclusive line of proof of the structure of the azoxy group. This proof consists of the preparation of a compound of the type:



If the azoxy group has the structure $-N=\overset{\overset{O}{\parallel}}{N}-$, then in the compound

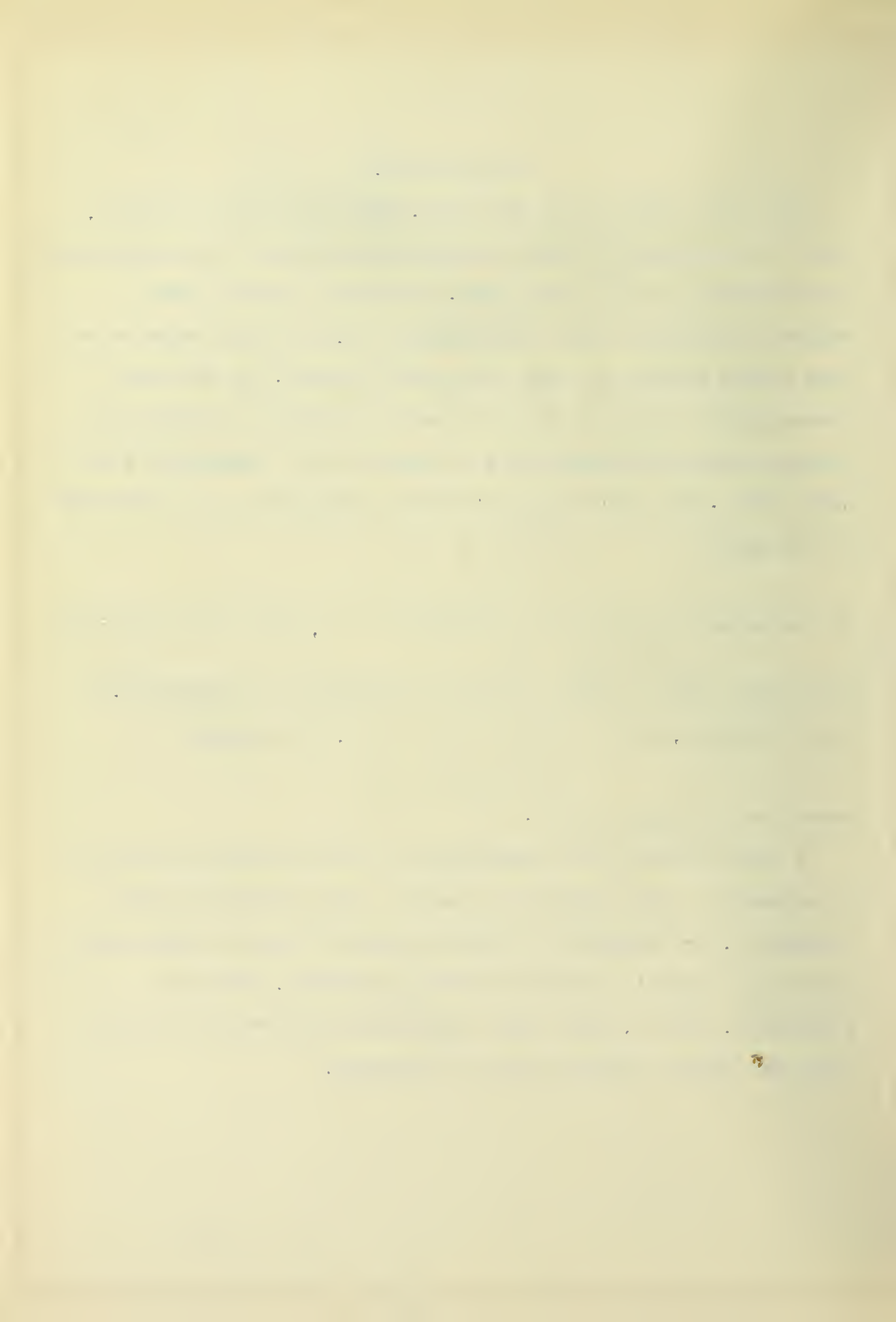


the carbon atom to which x and y are attached is asymmetric. On the other hand, if the structure is $-N-\overset{\overset{O}{\parallel}}{N}-$, the compound



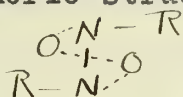
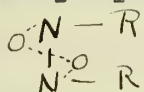
cannot be optically active.

It was realized at the beginning of the investigation that if a compound of type II could be resolved into optically active components, the structure of the azoxy group would be definitely proven and Angeli's conclusions fully verified. Failure of resolution, however, could mean that formula III was correct, or that the racemic mixture was not separated.



HISTORICAL AND THEORETICAL.

As late as 1894, Meyer and Jacobson(1)* stated that the structure of the azoxy group was far from being established, and that the structure usually assigned, $-\overset{\text{N}}{\underset{\text{O}}{\text{N}}}-$ I, had no experimental proof. Other structures proposed were $-\overset{\text{N}}{\underset{\text{O}}{\text{N}}}-$ II, and $-\overset{\text{N}}{\underset{\text{O}}{\text{N}}}-$ III. Brühl(2), basing his conclusions upon molecular refraction data, favored II or III. His interpretation of data and the assumptions he made make his conclusions questionable.(3),(4). Hantzsch and Werner (5) proposed two stereoisomeric structures for the group.



In these formulas, O signifies half an oxygen atom. They based their work on the existence of the two forms of p-azoxytoluene prepared by Janovsky and Reimann(6) and Lumiere and Seyewetz(7). Later work by Hantzsch(8) and Bamberger (9) makes the existence of two forms of p-azoxytoluene doubtful. Bamberger worked with unsymmetrical oxyazoxybenzenes, which he at first thought existed in two forms. He finally concluded(10) that in the case of o-oxyazoxybenzene at least, one of the isomers was not a real azoxy compound. Reissert (11) claimed to have prepared two forms of azoxybenzene, but his work could not be duplicated by Angeli.

Lachmann (12) discredits the unsymmetrical structure of the azoxy group on the grounds that:

(a). Zinc ethyl reacts vigorously with nitrosobenzene but not with azoxybenzene,

(b). Azoxybenzene is isomeric with diphenylnitrosobenzene, but is much less reactive than the latter.

(c). Petit(13) points out that the formation of azoxy compounds by the oxidation of azo compounds is an exothermic reaction.

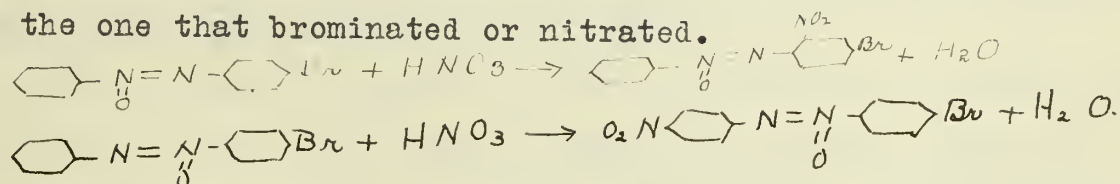
* These numbers refer to articles listed in the bibliography.

3.

All the oxides of nitrogen, on the other hand, have a negative heat of formation.

A. Angeli and his co-workers (14) favors the unsymmetrical structure $\text{N}=\text{N}^{\text{O}}$. He has prepared a large series of isomeric forms of unsymmetrical azoxy compounds by oxidizing the corresponding azo compounds with 30% hydrogen peroxide. An example will show his general scheme of work:

p-bromazobenzene, upon oxidation with 30% hydrogen peroxide, yields α and β p-bromazoxybenzenes whose melting points are 73° and 84° respectively. The structure of the two forms was established by the action of bromine and of nitric acid upon the isomers. It was found that the nucleus attached to the trivalent nitrogen was the one that brominated or nitrated.

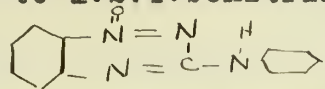


From the preparation of a series of similar isomers and from the fact that he was unable to prepare symmetrical azoxy compounds that existed in more than one form, Angeli concluded that the group has an unsymmetrical structure.

Campbell (15), using 58% hydrogen peroxide and p-ethoxyazobenzene, found that only one azoxy compound was formed and that the oxidation was not complete. He suggests that in some cases at least, Angeli's results are incorrect in that the isomers prepared were probably mixtures. Mattheus (16), using peracetic acid in acetic solution and p-brom and p-ethoxy azobenzenes arrived at much the same conclusions as Angeli.

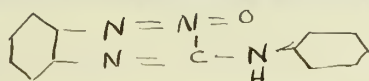
The work of Arndt (17) and of Arndt and Rosenan (18) on the preparation of cyclic azoxy compounds may be interpreted to support Angeli's theory. These compounds can be reduced to azo

and hydrazo compounds, and the latter can be oxidized with 33% hydrogen peroxide to give the original azoxy compound. O-nitro- α,β diphenylguanidine may be converted by boiling with sodium hydroxide to 1:2:4:benztriazine-3-anilino-1-oxide



melting point, 197°;

this can be reduced to 3-anilino-1:2:4:benztriazine (m.p. 197°), which, by means of 33% hydrogen peroxide and glacial acetic acid, can be oxidized to 3-anilino-1:2:4:benztriazine-2-oxide (m.p. 163°)



Both isomers behave alike when reduced.

Robinson(19) has shown that azoxyveratrole gives a mononitro compound while azoveratrole gives a symmetrical dinitro compound. This is in close agreement with Angeli's theory.

While the work of Angeli is rather conclusive in proving the structure of the azoxy group, it does not entirely close the question. His inability to prepare symmetrical azoxy compounds in two forms does not exclude their existence. Furthermore, as Campbell has pointed out(15), the purity of some of the isomeric compounds is questionable. In this investigation it was planned to try to solve the problem by the optical properties of a certain type of compound. It is possible the group may exist in different forms, in which case the change of structure may be noted in the change of optical properties.

The most promising compounds to use in preparing this type would be the o,o'-dinitro derivatives of benzilic or diphenylacetic acids, or of diphenylbrommethane. As the experimental work shows, our hopes were not fulfilled in these respects. At the time this investigation had to be closed, o,o'-dinitro-p,p'-

diamino-diphenylmethane and its azoxy derivative seemed to be the most promising compounds to use in continuing the work.

EXPERIMENTAL.

PREPARATION OF NITROGEN PENTOXIDE. Nitrogen pentoxide was prepared in a manner similar to the method of Berthelot(20). Into a liter glass retort fitted with either a glass or asbestos stopper, place 85g. of phosphorus pentoxide. Protect the open end of the retort with a calcium chloride tube. Place the retort in a freezing mixture and slowly add 60cc. of fuming nitric acid (sp.gr. 1.52), in such a manner that it is evenly distributed over the phosphorus pentoxide. Do not let the contents of the retort rise above 0°. The acid may be added from a dropping funnel. After all the acid has been added, the material in the retort should be very thick and viscous and nearly all the phosphorus pentoxide wetted. Then place the retort on a steam cone, remove the calcium chloride tube, and attach in its place a weighed Erlenmeyer flask so that the end of the retort almost reaches the bottom of the flask. Asbestos paper can be used to form a loose-fitting stopper for the receiving flask. Keep the latter cooled by means of a freezing mixture, and at the same time gently heat the retort on the steam cone to distill off the nitrogen pentoxide. The process is somewhat slow and generally requires about two hours. Do not heat too vigorously and do not allow any water to enter either the retort or the receiving flask. During the latter part of the distillation, some liquid distills over and mixes with the white crystals of nitrogen pentoxide which form on the sides of the receiving flask.

This is drained off as much as possible and may be used in the fuming nitric acid of the next run. The liquid is said to have the formula $2\text{N}_2\text{O}_5\cdot\text{H}_2\text{O}$. After draining off the liquid, the flask and "wet" nitrogen pentoxide are weighed to determine the amount of pentoxide obtained. The best yield we got was 50g. of "wet" pentoxide from 85g. of phosphorus pentoxide and 90g. of fuming nitric acid (sp. gr. 1.52).

PREPARATION OF ACETYLNITRATE. To the nitrogen pentoxide is added two or three times its weight of acetic anhydride. The former dissolves immediately with very little evolution of heat. In most cases it is not necessary to isolate the acetylnitrate, as it is used in acetic anhydride solution. The solution should be kept in a cool, dark place if stored for any length of time. Pictet and Khotinsky (21) state that acetylnitrate is a powerful nitrating agent and gives mainly ortho-nitrated products.

ATTEMPTED NITRATION OF BENZILIC ACID WITH ACETYLNITRATE.

80g. of benzilic acid were dissolved in 160 cc of acetic anhydride, the solution cooled to -5° , and to it added, slowly and with shaking, acetylnitrate solution, also cooled to -5° . The temperature of the benzilic acid solution was not allowed to rise above 0° . To each mol of benzilic acid was added, as nearly as could be ascertained, two mols of acetylnitrate. After the latter had been added, the solution was allowed to stand at 0° for half an hour, and then poured into ten volumes of ice-water. A brownish oil was obtained, which, after being washed with water, finally solidified. The solid product was almost entirely benzophenone, as shown by its melting point, 48° , and the melting point of its phenylhydrazone, 137° . 54g., i.e., 84% of the theory, of benzophenone were isolated.

PREPARATION OF DIPHENYLACETIC ACID(22).

Having seen that benzilic acid was oxidized rather than nitrated by acetylnitrate, it was next thought desirable to attempt nitrating diphenylacetic acid. The latter was prepared as follows:

Place in a liter flask:

100g. benzilic acid

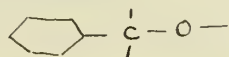
25cc hydroiodic acid

25g. red phosphorus

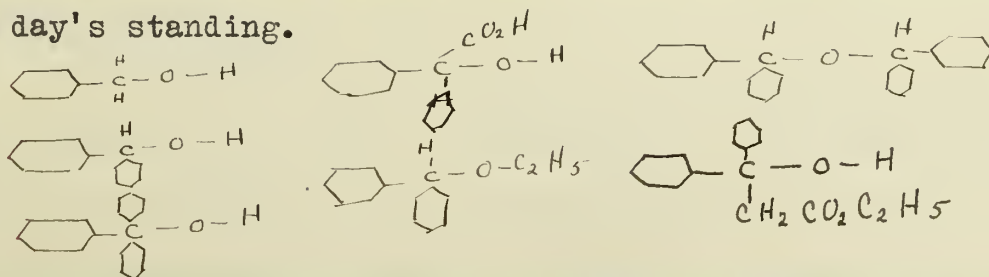
400cc glacial acetic acid.

Reflux two hours, filter, dilute filtrate to 1500cc with cold water. Diphenylacetic acid precipitates, is filtered off, and washed with cold water. It may be recrystallized from alcohol or hot water. yield, 92g.; i.e.; practically quantitative.

(Note: Benzilic acid, with cold, concentrated sulfuric acid, gives a red color; diphenyl acetic acid, under the same conditions, gives no color. This test can be applied to determine if reduction is complete. From qualitative tests, it seems that by this method one part of benzilic acid can be detected in at least 500 parts of diphenylacetic acid. The red color with cold, concentrated sulfuric acid seems to be given whenever there is the following grouping in the molecule:



All the following compounds were found to give the color except the last one, which gave a green color which turned red after a day's standing.



NITRATION OF DIPHENYLACETIC ACID WITH ACETYLNITRATE,

90g. of diphenylacetic acid were dissolved in 150cc of acetic anhydride and nitrated in a way analogous to the method described above for benzilic acid. After half an hour, the mixture was poured into ten volumes of ice-water. A reddish brown, viscous oil resulted. This product was treated with boiling alcohol; only the first two 100cc alcoholic extracts deposited appreciable amounts of solids upon cooling. The residue was then treated with boiling glacial acetic acid. The first six or eight 100cc extracts gave solids upon cooling, but the later ones gave products of increasing gumminess. The solids from the alcoholic and acetic acid extracts were combined, dissolved in alcohol, and an attempt made to fractionally crystallize the product. Evidently the solids were a complex mixture, as each crop of product melted over a range different from the others. The melting points of the various fractions ranged from 155° to 250°. The higher melting fractions were the more soluble in alcohol. The color ranged from light yellow in the case of the high melting fractions to brown in the lower melting parts. Evidently a portion was alkali-soluble, but no satisfactory separation could be made on this basis. The alkaline solution was opaque like some emulsions, and, upon acidification, lost but little of its opaqueness and deposited a very gummy residue.

This line of investigation seemed so little promising that it was dropped.

In nitrating benzilic acid with acetylnitrate, there is much oxidation; in the case of diphenylacetic acid, there apparently is some oxidation. It was then thought that diphenyl chlor- or brom-methane would probably nitrate more readily and oxidize less



easily. Diphenylbrommethane, being a solid, was chosen. We first tried to prepare it from benzhydrol and hydrobromic acid in alcoholic solution. The benzhydrol was prepared by the reduction of benzophenone in alcoholic solution by means of potassium hydroxide and zinc dust.

PREPARATION OF BENZHYDROL. Several runs were made. It was found that by using the same proportions thruout, 25g. runs gave much better results than larger amounts (100-200g.). Unless otherwise noted, the benzophenone was dissolved in absolute alcohol to which the potassium hydroxide had been added, either as a very concentrated aqueous solution, or as the solid and then dissolved in the alcohol. The solution was then heated to Boiling and the zinc dust added in lg. portions thru the reflux condenser.

Summary of the runs:

I. 200g. potassium hydroxide

2 liters of absolute alcohol

200g. of benzophenone

250g. of zinc dust.

The potassium hydroxide was first dissolved in the alcohol, the benzophenone then added, and the solution brought to a boil. The solution was stirred by means of a mechanical stirrer during all the time it was in the reaction flask. As soon as boiling began, the zinc dust was added. This process took about twenty minutes. The solution was refluxed for an hour, filtered while hot, and the residue washed twice with hot alcohol. Care had to be taken that the zinc residue did not become dry during the filtering, as under these conditions it burned. The filtrate

and washings were then poured into five volumes of ice-water.

The product separated as a very gummy, chocolate-brown mass, which was purified by vacuum distillation. Boiling point, $175-180/18-20$ mm. Yield, 180g, or 90%.

II. 150g. of potassium hydroxide dissolved in 50cc of water

1 liter of absolute alcohol

150g. of benzophenone purified by vacuum distillation

175g. of zinc dust.

The reaction was carried out as described above, except that the solution was not stirred. The product was almost as brown as the first run, and when vacuum distilled, boiled over a very wide range. The following products were identified in the various fractions of the distillate: unchanged benzophenone, m.p. 48° ; benzhydrol, m.p. 68° ; diphenylmethane, m.p. 26° ; and tetraphenylethane, the 1,1,2,2, compound, m.p. 209° . So complex was the mixture that it was thought not worth while to make a complete separation.

The following series of small runs were made to determine the effect of the concentration of alkali, time of boiling, etc. In no case was the reaction mixture stirred. The zinc dust was added during the course of five minutes. After refluxing, the reaction mixture was poured into ice-water as described above.

III. 53cc of an aqueous solution of potassium hydroxide; contained

24g. of the solid

200cc of absolute alcohol

25g. of purified benzophenone

30g. of zinc dust.

Mixture refluxed half an hour. Yield, 25g., 99%, of pure white product that melted $62-65^{\circ}$; the melting point of pure benzhydrol is 68° . When recrystallized from alcohol, the product melted at 68° .

IV. 150cc of absolute alcohol

53cc potassium hydroxide solution (24 g.of solid)

25g.benzophenone (not purified,but of good quality)

30g. of zinc dust.

Mixture refluxed half an hour and treated as above.Yield,25g.

Quality similar to run III.

V. 100cc of absolute alcohol

53cc of potassium hydroxide solution (24g. of solid)

25g. of purified benzophenone

30g. of zinc dust.

Yield,same as run III.

VI. 150cc of 95% alcohol

25g. potassium hydroxide in 15cc of water

25g. purified benzophenone

30g. of zinc dust.

Mixture refluxed for two hours,allowed to stand four days,
heated to boiling,and treated as above.Yield,same as run III.

VII. 500cc Of 95% alcohol

100g. of potassium hydroxide in 40cc of water

94g. of purified benzophenone

100g. of zinc dust.

Mixture refluxed for forty minutes,not stirred,and treated as
outlined above.Yield,93g. of very yellowish product that had to
be vacuum distilled.

From these results,it seems as if the size of the run and not
the concentration of the alkali or time of refluxing govern the
quality of the product. We have no explanation to offer for
this behavior.

ACTION OF HYDROBROMIC ACID ON BENZHYDROL AND BENZHYDROL ETHERS.

Attempts were made to prepare diphenylbrommethane by the action of 48% hydrobromic acid on benzhydrol in alcoholic solution(23). The first run was made by dissolving 100g. of benzhydrol in 500cc of 95% alcohol, adding 125cc of 48% hydrobromic acid, refluxing half an hour, and then allowing the solution to stand for ten hours. A yellow, oily product separated at the bottom of the mixture. After repeated washings with cold water, this product was found to retain only traces of halogen, It could not be solidified, even by cooling to -15° . When vacuum distilled, it yielded a colorless oil which boiled at $174/25\text{mm}$. The purified product was halogen free and could not be solidified at -15° ; yield, 96g.

The second run was made similar to the first except that the solution was allowed to stand at room temperature for twelve hours and was not refluxed. Two layers separated as before and the product obtained was like that from the first run. As the boiling point of the product did not correspond to that of benzhydrol and as it contained no halogen, the compound was neither benzhydrol or diphenylbrommethane. It was finally identified as benzhydrol ethyl ether by its boiling point of 287° at atmospheric pressure.

As this ether could not be used in this work, we tried to split it with hydrobromic acid and with hydriodic acid in hope of getting either the halide of benzhydrol. 50cc of the ether were refluxed four hours with 200cc of 48% hydrobromic acid. A solid product was obtained, which, after recrystallization from alcohol, melted at 109° . This product contained no halogen. Evidently it was benzhydrol ether. Neither this ether nor the

benzhydrol ethyl ether could be split with hydriodic acid, iodine, and red phosphorus.

We were suprised to find ether formation in the presence of so much water, and made the following runs to see to what extent this reaction would go:

10g. of benzhydrol

20cc of 48% hydrobromic acid

35 cc of water.

The mixture was refluxed half a n hour. 6 1/4 g. of purified benzhydrol ether were isolated. Evidently the ether formation takes place even in the presence of large amounts of water.

10g. of benzhydrol

20cc. of 48% hydrobromic acid

50cc of benzene.

The mixture was refluxed half an hour. Three grams of purified benzhydrol ether ~~were~~ isolated but no attempt was made to isolate all the product.

ACTION OF HYDROCHLORIC ACID ON BENZHYDROL AND NITRATION OF THE PRODUCT. One run was made using hydrochloric acid instead of hydrobromic:

60g. of benzhydrol

120cc of alcohol

600cc of concentrated hydrochloric acid

The reaction mixture was allowed to stand at room temperature for six hours and the bottom layer then separated and vacuum distilled. 55g. of product boiling from 173° to 195° at 25mm. was obtained. This product gave a qualitative test for halogen and solidified in a freezing mixture but had no definite

melting point. It was assumed to be diphenylchlormethane and was nitrated with acetylnitrate as described under benzilic acid above. A yellow, oily product was obtained, which, after a month's standing, deposited white crystals. These were identified as benzhydrol ether. This may be taken to mean that the original product contained benzhydrol ether, benzhydrol ethyl ether, and possibly diphenylchlormethane. After the isolation of benzhydrol ether from the nitration product, the yellow, oily residue was discarded, as it was thought a dinitro compound of diphenylchlormethane would be a solid.

PREPARATION AND NITRATION OF DIPHENYLBROMMETHANE. Diphenylbrommethane was prepared by slowly adding 105g of bromine to 110g. of diphenylmethane. The latter was put in a 500cc flask and heated to 110 in an oil bath. The contents of the flask were vigorously shaken after the addition of each drop of bromine. The latter was added from a dropping funnel. After all the bromine had been added, the reaction mixture was allowed to cool and was then recrystallized from petroleum ether. ⁽²⁴⁾ 80g. of pure product were isolated; more could have been obtained, but we did not take the time to do so. The 80g. of pure product were nitrated in acetic anhydride solution with acetylnitrate solution at -5° to 0° , as described under benzilic acid. A dark red, oily product was obtained which was soluble in hot benzene. No solid product, however, could be crystallized from this solvent. At this point acetylnitrate as a nitrating agent was abandoned.

PREPARATION OF p,p'-DIAMINO-DIPHENYLMETHANE. As the nitration with acetylnitrate did not give the desired type of compound, the preparation of o,o'-dinitro-p,p'-diamino-diphenylmethane

was carried out.

The first step is the preparation of p,p,diamino-diphenylmethane from anhydro-formaldehyd-aniline ,aniline,and aniline hydrochloride(25) . 250cc of formalin (40%) was diluted to four liters with water,and to this solution was added,during half an hour,250cc of aniline.The solution was stirred continually by a mechanical stirrer during the adding of the aniline and the stirring continued at room temperature for three hours afterward. The white,solid anhydro-formaldehyd-aniline was then filtered off,washed with water,put into a 5-liter flask,and to it added 300cc of aniline and 400g. of aniline hydrochloride.The mixture was then placed on a steam cone for 36 hours (later experiments showed that 24 hours were enough),then was treated with 150g. of sodium hydroxide in 500cc of water,and the mixture steam distilled until no more aniline came over.The free amine that remained was then washed with hot water and vacuum distilled. Yield,295g.,boiling at 255°-265°/18-20mm.

According to King(26),this product consists of nine parts of p,p,diamino-diphenylmethane and one part of the p,o',isomer. NITRATION OF p,p,DIAMINO-DIPHENYLMETHANE⁽²⁷⁾ The distilled amine, 200g.,was dissolved in three kilos of concentrated sulfuric acid,the solution cooled to 0°,and to it added 90cc of fuming nitric acid (sp.gr.1.5) in 100 cc of concentrated sulfuric acid.During this process the solution was stirred by means of a mechanical stirrer and the nitric acid added slowly enough so that the temperature did not rise above 0°.Stirring was continued two hours after the addition of the nitric acid and then the reaction mixture was poured into ten liters of ice-water.The acid was then neutralized with sodium carbonate,

care being taken that the temperature did not rise above 40°. When a slight excess of carbonate had been added, the product was filtered off and washed thoroughly with water. The best way we found to purify the product was to dissolve it in hot hydrochloric acid, filter, cool the filtrate to 10° or lower, and then precipitate the amine by adding dilute ammonia and at the same time stir very vigorously. During the addition of the ammonia, the temperature should be kept low. The precipitated amine is then extracted with a limited quantity of boiling alcohol; 400cc per 100g. of amine was found quite satisfactory. The insoluble portion is practically pure o,o'-dinitro-p,p'-diamino-diphenylmethane, and melts at 202°.

PREPARATION OF p,p'-DIBROM- AND p,BBOM-p'-HYDROXY- o,o'-DINITRO-DIPHENYLMETHANES. 50g. of the nitrated amine were dissolved in 150cc of concentrated hydrobromic acid and 100cc of water and filtered. The filtrate was cooled to 0°, and to it added 24g. of sodium nitrite dissolved in fifty cc of water. The diazonium salt was then added, with stirring, to a solution made by boiling 125g. of copper sulphate and 180g. of potassium bromide in 800cc of water with copper turnings until the solution was colorless. The latter was also cooled to 0°, and during the time of adding the diazonium solution, the temperature was not allowed to rise above 1°. Stirring was continued for half an hour and then the temperature allowed to rise to 25°. The product was then filtered off and the excess cuprous bromide dissolved out with hydrochloric acid. The material left after this treatment was refluxed with 400cc of alcohol for half an hour

and filtered. The insoluble portion consisted mainly of what probably was p-bromop-hydroxy-o,o' dinitro-diphenyl methane. This compound was not obtained in a pure condition and melted from 95° to 100°.

Analysis: bromine determined by Volhard method after fusion of the sample with sodium peroxide.

0.5109g. required 14.5 cc of 0.104 N silver nitrate solution, making the sample contain 24.1% bromine.

$C_{13}H_9O_5N_2Br$ contains, 22.6% bromine.

The analysis of the crude compound indicated that it contained but little of the dibrom compound, so it was not purified.

By adding half of its volume of water to the alcoholic filtrate described above, the solution became milky and upon standing, deposited yellowish crystals, which, according to their bromine content, were mainly the dibrom compound. Only two grams of these crystals were isolated; these we know were not pure and melted from 120° to 125°.

Analysis: 0.5676g. required 24.7cc of 0.104 N silver nitrate solution, i.e., 36.1% bromine.

$C_{13}H_9O_4N_2Br_2$ is 38.4% bromine.

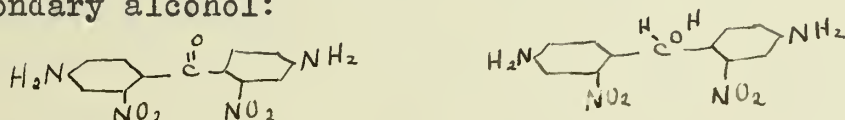
Another run was made using a suspension of cuprous bromide instead of the reduced copper solution described in the notes on the first run. The cuprous bromide was prepared by passing sulfur dioxide thru a solution of copper sulphate and potassium bromide, then filtering and washing the product. In this run no dibrom compound could be isolated. Because of the poor yields, no more attempts were made to prepare the dibrom compound.

Attempts were made to reduce the impure monobrom compound

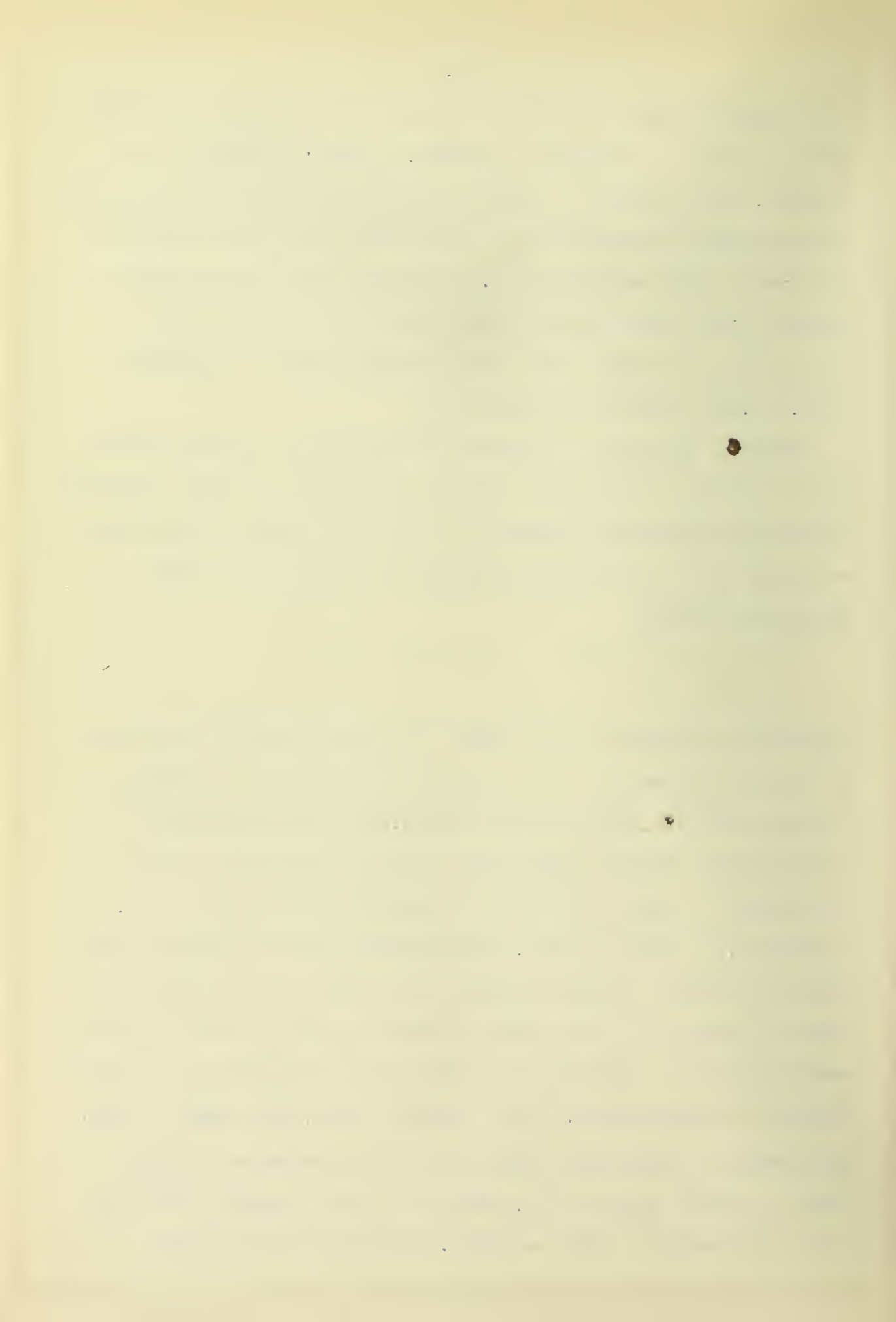
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to the azo or azoxy derivative by means of potassium hydroxide and zinc dust in alcoholic solution, by means of sodium and alcohol, and by means of sodium methylate. In all cases amorphous, reddish-brown products that did not melt but which carbonized from 200° to 300° were obtained. The impure dibrom compound was treated with sodium in alcoholic solution but the product obtained was somewhat like that obtained from the monobrom compound, and could not be purified.

King(26) describes a method of reducing the nitrated amine to the corresponding azoxy compound by means of sodium sulfide in alcoholic solution. We intended to try this method of preparing an azoxy derivative after oxidizing the amine to a ketone or secondary alcohol:



ATTEMPTED OXIDATION OF THE AMINE WITH LEAD PEROXIDE. We tried to oxidize the amine to the alcohol by the method of Mühlau and Heintze (28), using lead peroxide. The dihydrochloride of the amine we obtained free from excess hydrochloric acid by dissolving the amine in hot, concentrated hydrochloric acid, filtering, allowing to cool, and filtering off the hydrochloride which separated out. This hydrochloride was then dissolved as much as possible in hot water, allowed to cool, filtered, and the amount of amine determined in 100cc of the filtrate by precipitating it with ammonia. In the solution used, there were 2 1/4g. per 100cc of solution. To 680cc of this solution were added 6cc of glacial acetic acid, cooled to 0°, and treated with 12g. of finely powdered lead peroxide. The solution was shaken



vigorously for five minutes, and then divided into two parts. To the first part was added 8g. of crystalline sodium sulphate in solution, and the reaction mixture filtered. The amine in the filtrate was precipitated with ammonia, washed, and dried. A mixed melting point showed that it had not been changed. The other portion of the solution was allowed to stand with the peroxide for half an hour, was occasionally shaken, and then treated as the first portion. In this case too, the amine was found to be unchanged.

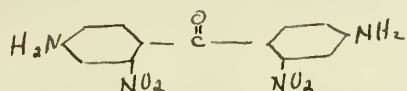
ACTION OF CHROMIC ACID UPON THE AMINE HYDROCHLORIDE. A strongly acid solution of the amine hydrochloride was treated, when warm, with enough chromic acid to oxidize it to the keto compound.

An insoluble, reddish-brown precipitate formed when the chromic acid was added. This precipitate contained chromium, and may be a chromate salt of the amine, but was not further investigated.

PREPARATION OF THE DIACETYL DERIVATIVE OF p,p,DIAMINO-o,o'-DINITRO-DIPHENYLMETHANE. 50g. of the free amine were treated with 100cc of acetic anhydride. After the reaction mixture had cooled, the semisolid mass was poured into ice-water and washed free from acid. The product, when recrystallized from alcohol, melted at 238°, and from its method of preparation, was thought to be the diacetyl derivative of the amine. It is fairly soluble in hot alcohol and very soluble in glacial acetic acid. When saponified with 25% sulfuric acid, it yields the original amine.

ATTEMPTED OXIDATION OF THE DIACETYL DERIVATIVE. Attempts were made to oxidize the diacetyl derivative in boiling acetic acid solution by means of sodium dichromate, of chromic acid, and of potassium permanganate in acetic acid solution. In each case

about 110% of the theoretical amount of oxidizing agent necessary to oxidize the amine to the keto compound



were used. The oxidizing agents were reduced, but when the product was recrystallized from alcohol, in every case it was found to be unchanged.

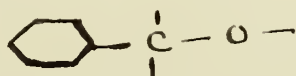
Time did not permit further experimental work, but at the end of the investigation it seemed that the following lines of attack may yield the desired results:

I. It may be possible to substitute one of the hydrogens of the aliphatic carbon with bromine and then reduce to the corresponding azoxy derivative.

II. The azoxy derivative may first be prepared and then the aliphatic carbon atom be oxidized, or brominated.

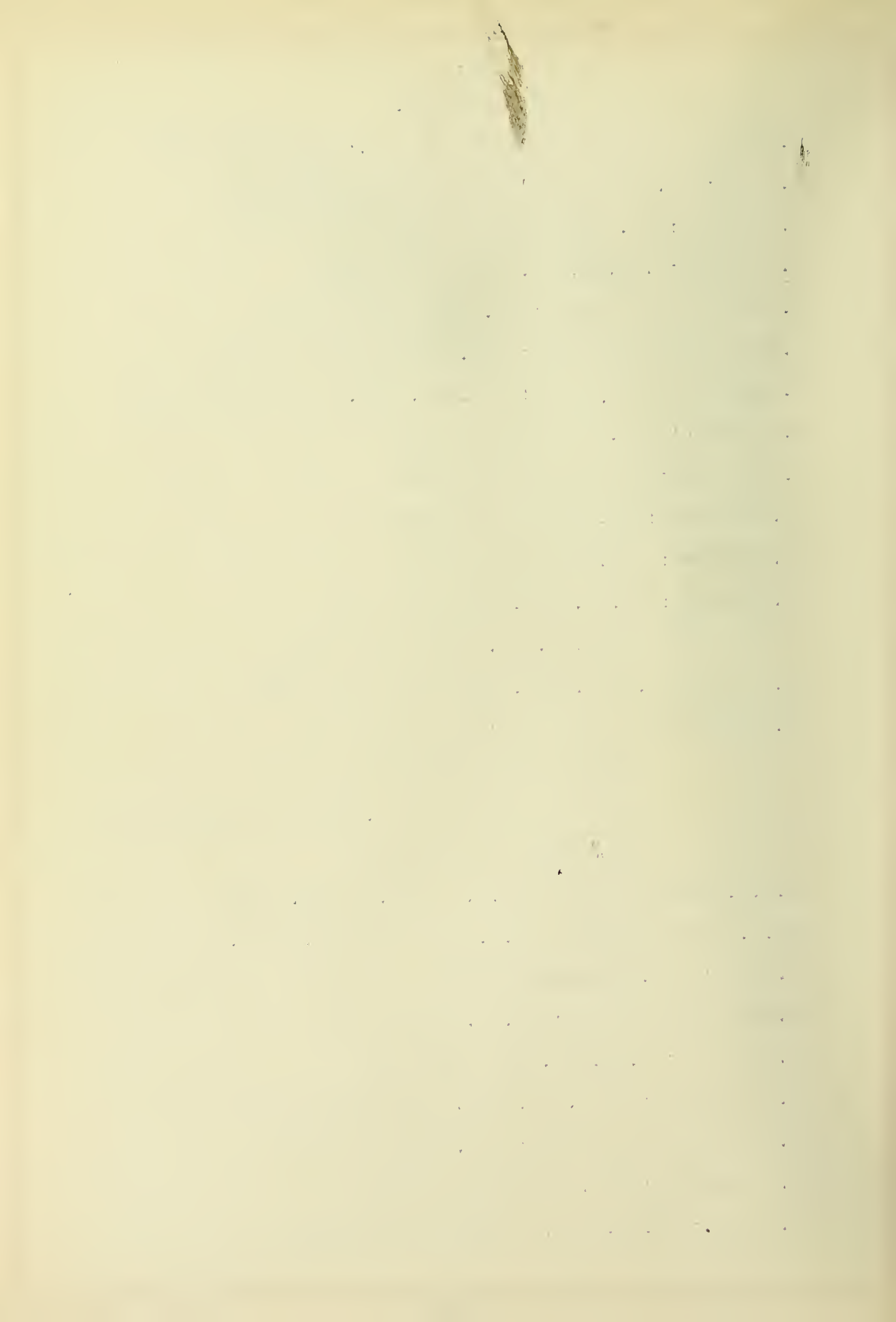
SUMMARY.

1. Acetyl nitrate has a strongly oxidizing effect upon benzoic acid, converting it mainly to benzophenone.
2. No definite products could be isolated from the nitration of diphenylacetic acid and of diphenylmethane with acetyl nitrate.
3. Benzyl ethyl ether and benzyl ethyl ether are readily formed from the corresponding alcohols in the presence of hydrobromic acid.
4. p,p,diamino-o,o',dinitro-o-diphenylmethane was prepared and unsuccessful attempts were made to prepare the corresponding secondary alcohol and keto derivatives.
5. p,p,dibrom- and p,brom-p,hydroxy derivatives of o,o',dinitro-diphenylmethane were prepared in an impure condition and attempts made to reduce these compounds to the corresponding amino or azoxy derivatives.
6. The diacetyl derivative of p,p,diamino-o,o',dinitro-diphenylmethane was prepared and attempts made to oxidize it to the keto derivative.
7. Lack of time prevented the preparation of the type of compound desired in demonstrating the structure of the ester group.
8. A color reaction was discovered which may be specific for the grouping:



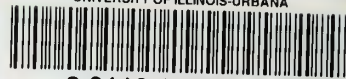
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